



Short communication

Sulfur/lithium-insertion compound composite cathodes for Li–S batteries

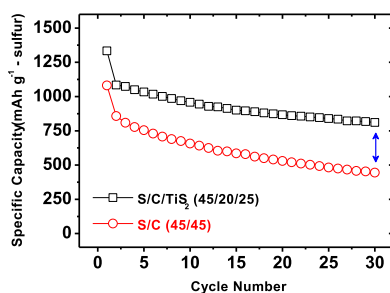
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HIGHLIGHTS

- Lithium-insertion compounds can reduce the carbon content in Li–S cells.
- $\text{VO}_2(\text{B})$ is not compatible with glyme-based electrolyte but TiS_2 is.
- TiS_2 is quite conductive and able to work in the mid-voltage range as sulfur.
- TiS_2 promotes active material dispersion and enhances the capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 April 2014

Received in revised form

28 June 2014

Accepted 15 July 2014

Available online 22 July 2014

Keywords:

Lithium–sulfur batteries

Cathode materials

Sulfur composite cathodes

Vanadium oxide

Titanium disulfide

ABSTRACT

A part of carbon additives in sulfur cathodes is replaced by lithium-insertion compounds as they can contribute extra capacity and increase the overall energy density. Accordingly, $\text{VO}_2(\text{B})$ and TiS_2 were incorporated into sulfur cathodes as they can work within the same voltage window as that of sulfur. However, $\text{VO}_2(\text{B})$ was found to be incompatible with the glyme-based electrolytes that are usually used in Li–S cells, but TiS_2 performs well while coupled with sulfur. The S/C/ TiS_2 composite cathode delivers 252 mAh g^{-1} more than that of pristine sulfur cathode (1334 mAh g^{-1} vs. 1082 mAh g^{-1}). The increased capacity is not only due to the contribution by TiS_2 itself but also due to a better active-material dispersion and utilization. Serving as active reaction sites during cycling, TiS_2 suppresses agglomeration of sulfur and facilitates better ionic/electronic transport within the cathode structure. This composite cathode design provides another direction for Li–S batteries to improve the overall energy density.

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1. Introduction

Research in high-energy-density batteries has become dominant as the demand for energy storage is increasing in the fields of electric vehicles, grid storage, and portable electronics. Lithium–sulfur batteries stand out among the rest due to their high

theoretical capacity, low cost, and abundant sulfur resources [1]. Recent studies have focused mostly on the design of sulfur cathodes, such as carbon matrix modifications [2,3], various types of sulfur active materials [4,5], and new cell configurations [6]. These approaches overcome to some extent the drawbacks of high resistivity of sulfur and easy dissolution of intermediate polysulfide species. Major Li–S systems contain a certain amount of carbon additives which serve as electrical conductors and polysulfide adsorbents to improve active material utilization and capacity retention during cycling. However, a high carbon content results in

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a low sulfur active material percentage in the cathode, thereby diminishing the overall energy density of Li–S cells and the advantage of sulfur cathodes.

Our group proposed a composite cathode system consisting of sulfur and a lithium-insertion compound to reduce the amount of inactive carbon materials [6]. In this communication, two different insertion compounds are examined to replace a part of carbon in the cathode. $\text{VO}_2(\text{B})$ is known to be a good co-cathode material to reduce the irreversible capacity loss in the first cycle of lithium-rich layered oxide cathodes [7]. Titanium disulfide is the first cathode material used to demonstrate the rechargeable lithium battery concept, and it had been combined with sulfur as a hybrid cathode for lithium–sulfur batteries [8]. The work by Garsuch et al. on S/ TiS_2 cathodes reveals that the addition of titanium disulfide improves significantly the pulse power capability of Li–S cells [8]. Fig. 1 exhibits that both $\text{VO}_2(\text{B})$ and TiS_2 are capable of working within a mid-voltage range (1.5 V–3.0 V vs. Li^+/Li^0) that coincides with the working voltage of pure sulfur in lithium batteries [9]. This criterion is important because the co-cathode material needs to contribute extra capacity simultaneously during the electrochemical reaction of sulfur with lithium. Moreover, the lithium-insertion compounds must be able to work with the same electrolyte system as that for Li–S batteries.

2. Experimental

2.1. Preparation of sulfur/lithium-insertion compound cathodes

Pure sulfur used in this study was synthesized by a reaction between hydrochloric acid and sodium thiosulfate solution. $\text{VO}_2(\text{B})$ was synthesized via a hydrothermal process as reported before [7]. TiS_2 (99.8%; Stream Chemicals) was used as purchased. All the active materials were ground in a mortar before preparing the cathode slurries. The sulfur composite slurry was made by mixing the active material, Super P carbon, and polyvinylidene fluoride (PVDF; Kureha) binder together in an *N*-methylpyrrolidinone (NMP; Sigma–Aldrich) solution. Sulfur and binder contents were fixed at, respectively, 45 wt. % and 10 wt. %, and the remaining 45 wt. % was comprised of carbon and lithium-insertion compounds. The slurry was cast onto an aluminum foil with a doctor blade and dried in a vacuum oven overnight at 50 °C, followed by pressing with a roller machine and cutting into circular electrodes.

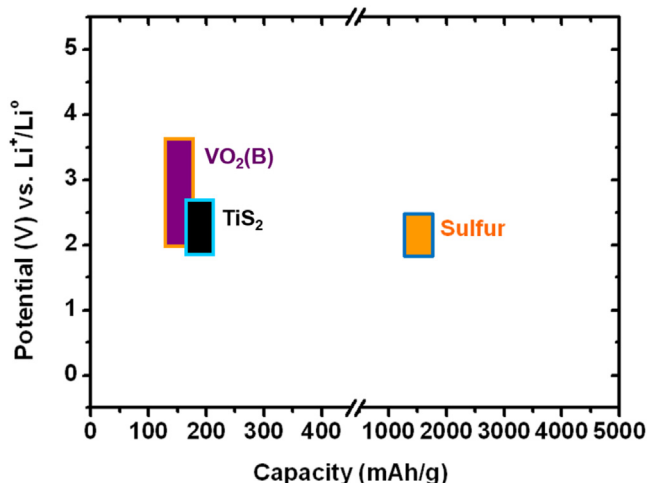


Fig. 1. Redox potential/capacity charts of cathode materials for lithium-ion batteries.

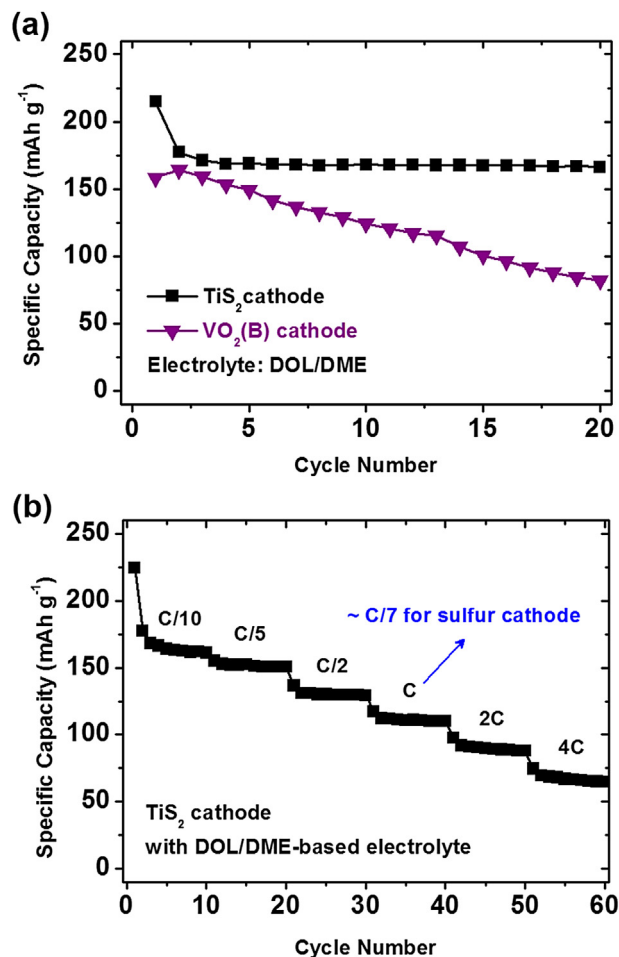


Fig. 2. (a) Cyclability of pure $\text{VO}_2(\text{B})$ and TiS_2 cathodes and (b) rate capability of pure TiS_2 cathode (here $1\text{C} = 240\text{ mA g}^{-1}$) in DME/DOL electrolyte.

2.2. Cell assembly

The electrolyte was made by adding 1.85 M LiCF_3SO_3 (Acros Organics) and 0.1 M LiNO_3 (Acros Organics) salt into a mixture of 1,2-dimethoxyethane (DME; Acros Organics) and 1,3-dioxolane (DOL; Acros Organics) (1:1, v/v). The Li–S cells were assembled with the prepared cathode disks, electrolyte, Celgard polypropylene separators, lithium anodes, and nickel foam spacers in CR2032 coin cells. The cell assembly was carried out in an Argon-filled glove box at room temperature with extremely low H_2O and O_2 concentrations (<0.6 ppm). Finally, the cells were crimped and taken out of the glove box for electrochemical analysis.

2.3. Materials and electrochemical characterization

Crystal-chemical characterization was carried out with a Philips X-ray diffractometer (PW 1830 + APD 3520) with Cu K α radiation. The microstructure and elemental analysis were conducted with a FEI Quanta 650 scanning electron microscope (SEM). The electrical resistivity of the electrodes was measured with a standard four-point probe method, equipped with a Keithley 2400 Source Meter. The charge/discharge profiles and cycle data were collected with a programmable Arbin battery cycler. The C rates and specific capacity were calculated based on the sulfur weight in the cathode. Electrochemical impedance spectra (EIS) were collected with a Solartron Impedance Analyzer (SI 1260 + SI 1287) from 1 MHz to

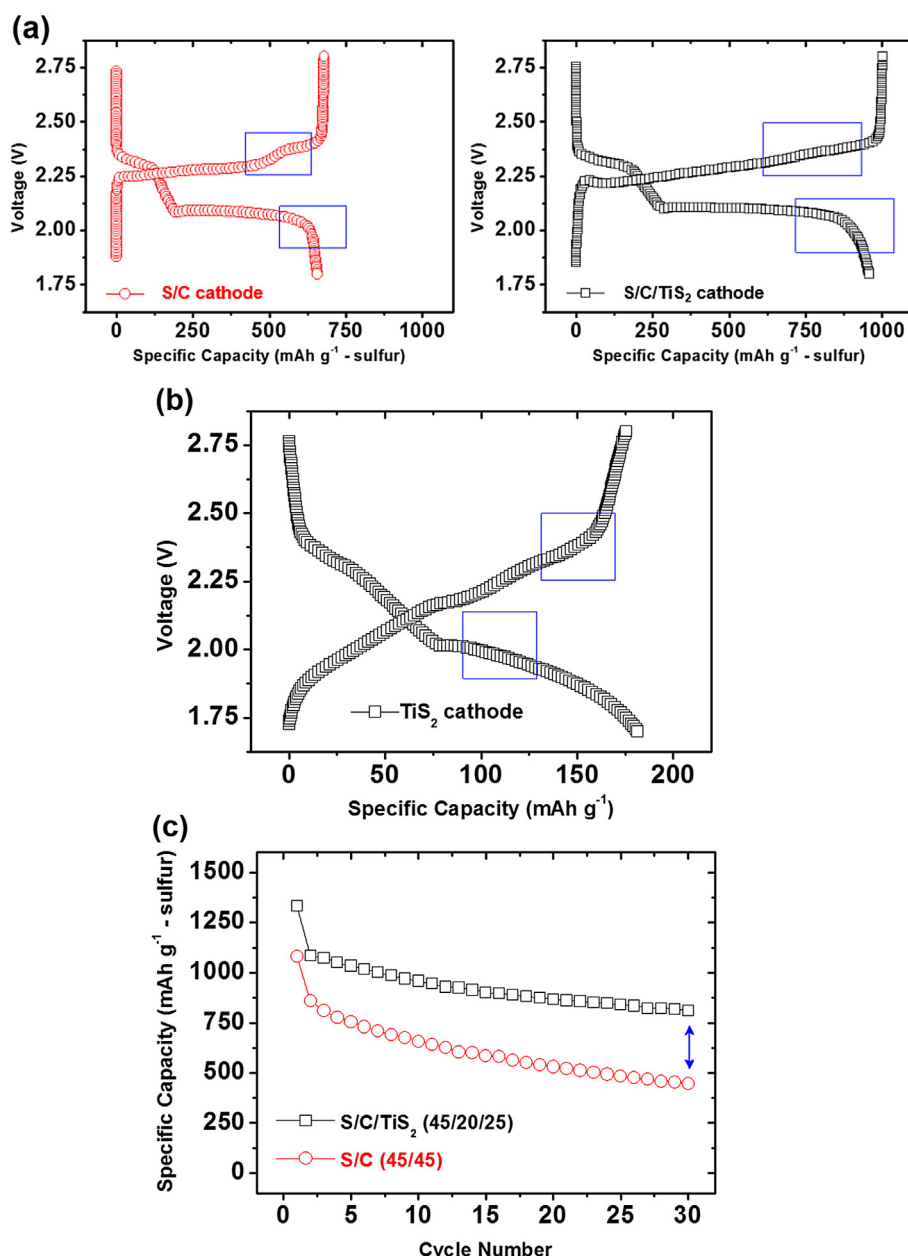


Fig. 3. (a) Comparison of the charge/discharge profiles of pristine S/C cathode and S/C/TiS₂ cathode at 10th cycle, (b) charge/discharge profiles of pure TiS₂ cathode, and (c) cyclability of pristine S/C cathode and S/C/TiS₂ cathode; the numbers in the legend refer to wt. % of the cathode (the remaining 10 wt. % is from PVDF binder). The C rate for the cathodes is C/10 (167.5 mA g⁻¹).

100 mHz with an AC voltage amplitude of 5 mV at the open-circuit voltage of the cells with Li metal foil as both auxiliary and reference electrodes.

3. Results and discussion

3.1. Compatibility of VO₂(B) and titanium disulfide in DME/DOL electrolyte

Before being used to replace carbon additives in sulfur cathodes, the lithium-insertion compounds have to be examined if they can be stably charged/discharged in the electrolyte of Li–S batteries. Therefore, pure VO₂(B) and TiS₂ cathodes were made (60 wt. % active materials +20 wt. % PVDF +20 wt. % Super P) and assembled in the cells with DME/DOL electrolyte. Although VO₂(B) can be

cycled in carbonate electrolyte, it is not suitable to be used with DME/DOL electrolyte due to irreversible redox reactions (Fig. 2(a)). When pure VO₂(B) is soaked in DME/DOL electrolyte, color change was observed with resting time goes, possibly due to active material dissolution [10]. This means VO₂(B) is incapable of being combined with sulfur as a co-cathode material, especially in DME/DOL electrolyte. In contrast, pure TiS₂ cathode stably delivers a capacity of ~170 mAh g⁻¹ in DME/DOL electrolyte in the voltage range of 1.7–2.8 V, making it a good candidate to be coupled with sulfur.

3.2. Cycle performance of sulfur/titanium disulfide cathodes

Knowing that titanium disulfide can potentially be a good co-cathode material for sulfur, we prepared the S/C/TiS₂ cathode by

Table 1
Actual capacity and degradation rate of pristine S/C cathode and S/C/TiS₂ cathode.

Cathode	First discharge capacity (mAh g ⁻¹)	Reversible discharge capacity after 30 cycles (mAh g ⁻¹)	Degradation rate per cycle
Pristine S/C cathode	1081	445	2.0%
S/C/TiS ₂ cathode	1000	608	1.3%

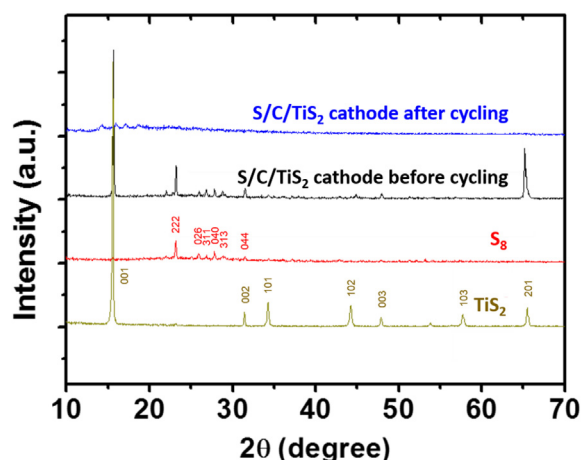


Fig. 4. XRD patterns of sulfur, TiS₂, and S/C/TiS₂ cathode before and after cycling.

replacing a part of carbon with TiS₂ (25 wt. %). Before cycling the composite cathode, rate capability test of the pure TiS₂ cathode (Fig. 2(b)) was carried out to determine the appropriate C rate that can be used for the composite cathode. TiS₂ could be cycled up to

240 mA g⁻¹ while still delivering a capacity of over 100 mAh g⁻¹, which equals to $\sim C/7$ for Li–S cells. Pure TiS₂ cathode can deliver about 120 mAh g⁻¹ within the same voltage window at 167.5 mA g⁻¹ ($C/10$ of Li–S batteries).

The charge/discharge profiles of the pristine S/C and S/C/TiS₂ composite cathodes are exhibited in Fig. 3(a). The shape changes in the voltage profiles of S/C/TiS₂ cathode can be easily observed at the regions indicated by a blue box in Fig. 3(a) (in web version), which coincides with the voltage range of TiS₂ (Fig. 3(b)). This confirms that TiS₂ also undergoes redox reaction with lithium along with the sulfur cathode. The S/C/TiS₂ composite cathode exhibits better cyclability and higher capacity than pristine S/C cathode shown in Fig. 3(c). It can be seen that the S/C/TiS₂ cathode offers 252 mAh g⁻¹ higher capacity than the S cathode without TiS₂. Interestingly, the increased capacity (252 mAh g⁻¹) exceeds the maximum value that TiS₂ is expected to contribute by itself (~ 67 mAh g⁻¹; calculated by the capacity of TiS₂ at the rate of 167.5 mA g⁻¹ \times TiS₂/S ratio of the electrode), implying that the addition of TiS₂ may also improve the sulfur utilization. Table 1 shows the actual capacity calculated based on the overall weight of the active materials, which includes S and TiS₂. The first discharge capacity is comparable to that of pristine S/C cathode, but its degradation rate is somewhat better than that of pristine S/C cathode. The incorporation of TiS₂ into the electrode does not substantially suppress the capacity degradation because the TiS₂ particles used in this study are large and non-porous; however, the capacity retention could be further improved by employing highly porous and nanostructured lithium-insertion compounds to assist polysulfide absorption. From the results of four-point probe resistivity measurements, it can be found that the S/C/TiS₂ composite cathode ($2.3 \times 10^3 \mu\Omega \times \text{cm}$) is more conductive than the pristine S/C cathode ($4.5 \times 10^3 \mu\Omega \times \text{cm}$). Thus, the S/C/TiS₂ composite cathode structure seems to offer better electron transport during cycling.

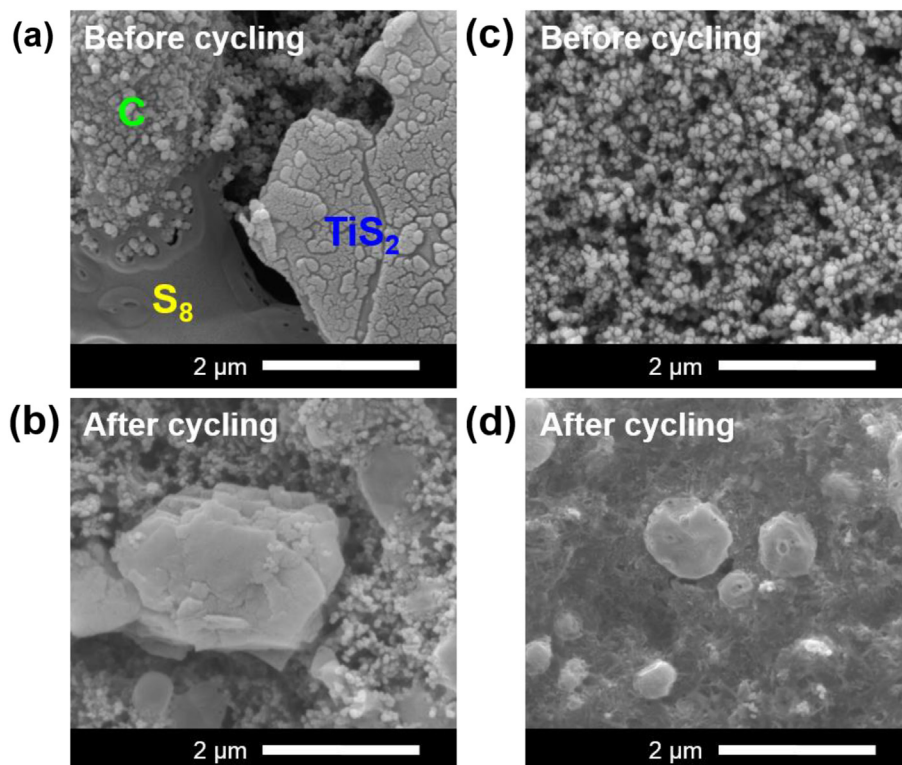


Fig. 5. SEM images of S/C/TiS₂ composite cathode (a) before cycling and (b) after cycling, and pristine S/C cathode (c) before cycling and (d) after cycling.

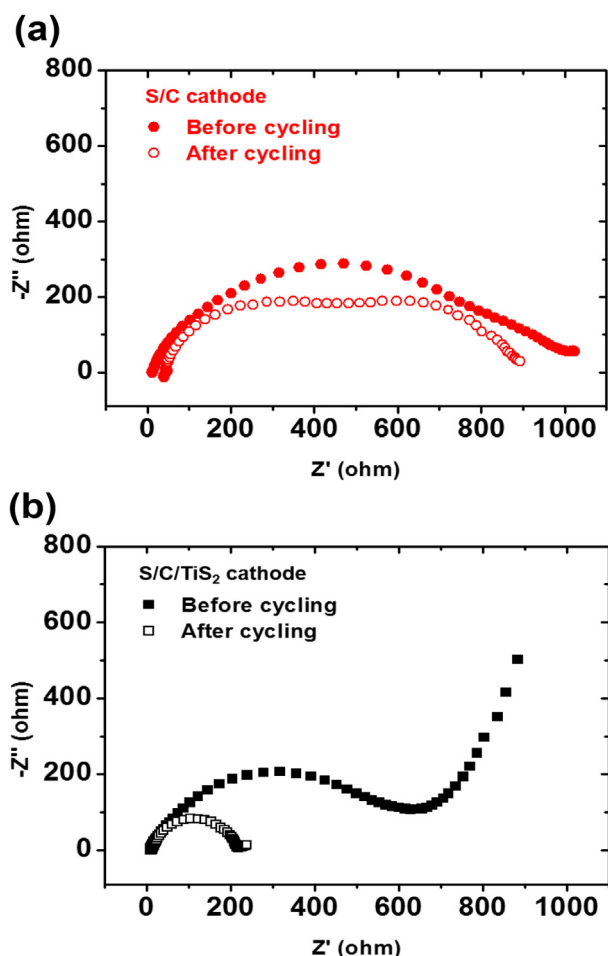


Fig. 6. EIS spectra of (a) S/C cathode before and after cycling and (b) S/C/TiS₂ cathode before and after cycling.

3.3. XRD, SEM, and EIS analysis of cycled electrodes

The XRD data shown in Fig. 4 reveal that the pure sulfur and TiS₂ used in this study are crystalline and match with the JCPDS files [11,12]. Before cycling, the S/C/TiS₂ cathode consists of both the crystalline phases of sulfur and TiS₂. However, after cycling, the composite cathode becomes relatively amorphous with a few very weak new peaks, which could not be identified; the transformation of crystallized S₈ to an amorphous structure is generally found in Li–S batteries [13]. The vanishing of TiS₂ peaks and the formation of weak new peaks could possibly be due to the interaction between TiS₂ and polysulfides. Fig. 5 compares the morphological differences of the S/C/TiS₂ and pristine S/C cathodes before and after cycling. The texture of TiS₂ is distinct as can be easily seen in the microstructure (Fig. 5(a)). After several cycles shown in Fig. 5(b), the S/C/TiS₂ cathode does not change much, maintaining its original structure. The pristine S/C cathode displays that the conductive carbon particles cover onto sulfur before cycling (Fig. 5(c)). However, the electrode exhibits totally different morphology after cycling (Fig. 5(d)), showing that sulfur agglomerates on the surface of the cathode and the conductive carbon cannot be clearly seen anymore. Once the carbon additive is isolated by the insulating sulfur, the active material utilization will decrease due to poor electron transport. Also, the dense aggregate in the structure may block ionic transport during charge/discharge. EIS spectra in Fig. 6

show that the difference between the S/C/TiS₂ cathode and S/C cathode is quite distinct. Before cycling, the S/C/TiS₂ cathode has lower internal resistance than the S/C cathode, so the sulfur utilization in the S/C/TiS₂ is better, leading to a higher first discharge capacity. The Nyquist plot of the S/C/TiS₂ cathode shrinks extensively after cycling because the polysulfides may migrate to electrochemically stable sites with cycling [14]. In contrast, the Nyquist plot of the S/C cathode remains the same size and it exhibits a bimodal impedance, which is believed to be charge-transfer resistance at the electrode/electrolyte interface and surface film resistance due to sulfur agglomeration [15,16]. As a result, the existence of TiS₂ seems to promote active-material dispersion and stabilize the cathode structure. The integrity and stability of the electrode structure are important criteria for the electrodes to offer long cycle life.

4. Conclusions

Unlike most of the cathode materials, the insulating sulfur needs a high content of conductive additives to improve the performance of Li–S batteries. However, adding too much of conductive, electrochemically inactive carbon to the electrode would reduce the overall energy density, losing the merit of adopting sulfur cathodes. Replacement of part of the conductive carbon additives with lithium-insertion compounds could somewhat overcome this difficulty. However, the incorporation of VO₂(B) was not successful as it could not be stably cycled with DME/DOL electrolyte. In contrast, the incorporation of TiS₂ as a co-cathode material is successful as TiS₂ is quite conductive, able to work in the mid-voltage range as sulfur, and capable of undergoing reversible lithium insertion reactions in glyme-based electrolyte. TiS₂ not only contributes to the capacity but also enhances the dispersion of sulfur and thereby its electrochemical utilization, and the latter seems to be a significant cause of the performance enhancement. The cell performance could be further improved by designing state-of-the-art TiS₂ with porous structure to accommodate the active sulfur and enhance polysulfide absorption. In conclusion, a good co-cathode material for sulfur cathodes must be capable of working within a mid-voltage range and stably cycling in the electrolyte of Li–S batteries.

Acknowledgments

This work was supported by Seven One Limited. The authors thank Chih-Liang Wang for the four-point probe measurements.

References

- [1] X. Ji, L.F. Nazar, *J. Mater. Chem.* 20 (2010) 9821.
- [2] X. Ji, K.T. Lee, L.F. Nazar, *Nat. Mater.* 8 (2009) 500.
- [3] N. Jayaprakash, J. Shen, S.S. Moganty, A. Corona, L.A. Archer, *Angew. Chem. Int. Ed.* 50 (2011) 5904.
- [4] Y. Fu, Y.-S. Su, A. Manthiram, *Angew. Chem. Int. Ed.* 52 (2013) 6930.
- [5] S. Xin, L. Gu, N. Zhao, Y. Yin, L. Zhou, Y. Guo, L. Wan, *J. Am. Chem. Soc.* 134 (2012) 18510.
- [6] A. Manthiram, Y. Fu, Y.-S. Su, *Acc. Chem. Res.* 46 (2012) 1125.
- [7] E.S. Lee, A. Manthiram, *J. Electrochem. Soc.* 158 (2011) A47.
- [8] A. Garsuch, S. Herzog, L. Montag, A. Krebs, K. Leitner, *ECS Electrochem. Lett.* 1 (2012) A24.
- [9] J.B. Goodenough, Y. Kim, *Chem. Mater.* 22 (2010) 587.
- [10] M. Zhang, J. Dahn, *J. Electrochem. Soc.* 143 (1996) 2730.
- [11] Y.-S. Su, A. Manthiram, *Electrochim. Acta* 77 (2012) 272.
- [12] J. Chen, S.-L. Li, Z.-L. Tao, F. Gao, *Chem. Commun.* 8 (2003) 980.
- [13] Y.V. Mikhaylik, J.R. Akridge, *J. Electrochem. Soc.* 151 (2004) A1969.
- [14] Y.-S. Su, Y. Fu, A. Manthiram, *Phys. Chem. Chem. Phys.* 14 (2012) 14495.
- [15] S.R. Narayanan, D.H. Shen, S. Surampudi, A.I. Attia, G. Halpert, *J. Electrochem. Soc.* 140 (1993) 1854.
- [16] L.X. Yuan, X.P. Qiu, L.Q. Chen, W.T. Zhu, *J. Power Sources* 189 (2009) 127.